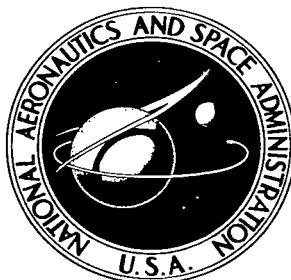


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A METHOD FOR COMPUTING
CHEMICAL-EQUILIBRIUM COMPOSITIONS
OF REACTING-GAS MIXTURES BY REDUCTION
TO A SINGLE ITERATION EQUATION

*by Wayne D. Erickson, Jane T. Kemper,
and Dennis O. Allison*

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SUMMARY

A method for computing the equilibrium chemical composition of a reacting gas mixture is presented wherein all the equilibrium and mass-balance equations are combined algebraically into one equation involving a single unknown. A comparison between this method and a widely used more general method shows that the unit computational speed of the present method can be as much as two orders of magnitude faster. This great advantage in computational speed is achieved at the expense of generality. The present method for computing equilibrium chemical compositions should be useful when applied to systems of intermediate complexity and where a large number of computations are required.

INTRODUCTION

A number of methods have been developed for computing the equilibrium chemical composition and thermodynamic properties of reacting gas mixtures. These methods employ various iteration schemes. Although the machine computation time required to obtain a single solution may be small, the machine computation time in flow-field problems that require a very large number of equilibrium composition calculations may be excessive. In that case, a series of empirical curve fits of the thermodynamic properties is sometimes used.

A study of three of the most widely used general methods for computing chemical-equilibrium compositions was carried out by Zeleznik and Gordon (ref. 1.) The study considered the methods of Brinkley (ref. 2), Huff, Gordon, and Morrell (ref. 3), and White, Johnson, and Dantzig (ref. 4) with regard to any computational advantage of one method over the other methods. The comparison showed that none of the methods indicated any significant computational advantage over the other two.

The present work outlines a method for computing the equilibrium chemical composition wherein the complete set of equilibrium and mass-balance equations are reduced to one equation involving a single unknown. A comparison between the present method and the more general method of White will show that a great advantage in computational speed is realized in the present method. As will be shown, this advantage is achieved at the expense of generality.

SYMBOLS

$a_{i,k}$	mass of kth element per mass of ith species
$\bar{a}_{i,k}$	number of atoms of kth element per molecule of ith species
$\frac{A_i}{RT}$	nondimensional Helmholtz free energy of ith species
$\frac{A}{RT}(x_1, x_2, \dots, x_I)$	nondimensional Helmholtz free energy of reacting gas mixture
$b_{k,k+1}$	mass ratio of kth element to the (k + 1)th element in the mixture, regardless of chemical species in which they appear
\bar{b}_k	total number of atomic weight units of element k per mass of mixture
c_i	mass fraction of species i in mixture
$c_1(n)$	nth approximation of c_1
d_l	indexed coefficients in equation (6)
$F(c_1)$	function defined by equation (6)
$F'(c_1)$	derivative of $F(c_1)$ (see eq. (8))
$\frac{F_i}{RT}$	nondimensional Gibbs free energy of ith species
$\frac{F}{RT}(x_1, x_2, \dots, x_I)$	nondimensional Gibbs free energy of reacting gas mixture

$\frac{\Delta F_{f,i}^0}{RT}$	nondimensional standard-state free energy of formation of species i at temperature T
i,I,j,J,k,K,l,L	integers
$K_{p,j}$	equilibrium constant in terms of partial pressures for reaction j
m	unit computational time, time/case
N	number of cases computed per run
p	pressure
R	universal gas constant
T	temperature
W_i	molecular weight of ith species
W	molecular weight of mixture
x_i	mole number of species i, $\frac{\text{Moles of species } i}{\text{Mass of mixture}}$
\bar{x}	mole number of mixture, $\frac{\text{Total moles of mixture}}{\text{Mass of mixture}}$
X_i	chemical symbol of species i where, for example, in equation (4) $X_1 = H$, $X_2 = O$, $X_3 = H_2$, etc.
β	mass-balance quantity defined by equation (22)
t_c	actual computational time (this time is exclusive of input and output times)
t_{in}	input time
t_{out}	output time
t_T	total machine time

$\nu_{i,j}$	stoichiometric coefficient of reactant species i in j th reaction
$\nu'_{i,j}$	stoichiometric coefficient of product species i in j th reaction
ρ	density of mixture
τ_j	modified equilibrium constant defined by equation (5)

Subscripts:

i	i th species
I	total number of species in mixture
j	j th reaction
J	total number of independent reactions that can be written for mixture
k	k th element
K	total number of elements in mixture
l	power series index in equation (6)
L	highest order power in equation (6)

EQUILIBRIUM COMPOSITION EQUATIONS

This section is concerned with the development of a technique for computing the equilibrium chemical composition of a reacting mixture at a given temperature, density, and set of mass restraints, wherein the solution for a single equation involving only one composition term is obtained. The solution for all the remaining species then are found by direct substitution. The general equations for an equilibrium reacting gas system involving an arbitrary number of species and chemical elements are presented, after which a specific set of equations are written for a reacting mixture of hydrogen and air.

General Equations

In an equilibrium reacting gas mixture containing I chemical species, which in turn are composed of K chemical elements, there are J independent and simultaneous

chemical reactions that can be written, such that $I = J + K$. Application of the conservation of mass for each of the k th chemical elements leads to the following K equations:

$$\frac{\sum_{i=1}^I a_{i,k} c_i}{\sum_{i=1}^I a_{i,k+1} c_i} = b_{k,k+1} \quad (k=1,2,\dots,K-1) \quad (1)$$

and

$$\sum_{i=1}^I c_i = 1 \quad (2)$$

The quantity $a_{i,k}$ represents the total mass of atoms of the k th element per mass of a molecule of the i th chemical species, $a_{i,k+1}$ is the corresponding quantity for the $(k+1)$ th element, and $b_{k,k+1}$ is defined as the mass ratio of the k th element to the $(k+1)$ th element in the mixture, regardless of the chemical species in which the element appears.

There are also J equilibrium expressions which can be written as

$$\prod_{i=1}^I c_i^{\nu'_{i,j} - \nu_{i,j}} = \tau_j^{-1} \quad (j = 1,2,\dots,J) \quad (3)$$

which correspond to the J independent chemical reactions containing species X_i ,

$$\sum_{i=1}^I \nu_{i,j} X_i \rightleftharpoons \sum_{i=1}^I \nu'_{i,j} X_i \quad (j = 1,2,\dots,J) \quad (4)$$

The quantity τ_j in equation (3) is a modified equilibrium constant which is a function of T and ρ ,

$$\tau_j^{-1} = K_{p,j} (\rho RT) \sum_{i=1}^I \nu_{i,j} - \nu'_{i,j} \prod_{i=1}^I w_i^{\nu'_{i,j} - \nu_{i,j}} \quad (j = 1,2,\dots,J) \quad (5)$$

where $K_{p,j}$ is the equilibrium constant in terms of partial pressures for the j th reaction.

Equations (1), (2), and (3) constitute I independent equations involving as many unknown c_i . The present technique for computing the chemical composition at a specified temperature, density, and mass restraints (specific mass restraints are reflected through $a_{i,k}$, $a_{i,k+1}$, and $b_{k,k+1}$ of equation (1)) first entails writing down the K equations suggested by equations (1) and (2). These K equations contain all I unknowns, namely, the mass fractions c_i . The J equilibrium equations given by equation (3) are then substituted into these K equations for the mass constraints in order to reduce the I unknowns by J so that a modified set of K equations is obtained containing only K unknowns, for example, c_1, c_2, \dots, c_K . These resulting K equations are then combined algebraically in such a way as to obtain a single equation containing only one unknown, for example, c_1 , where c_1 is the mass fraction of an arbitrarily chosen species 1. (See appendix for the details of the algebraic reduction.) This single equation can be expressed as

$$F(c_1) = \sum_{l=0}^L d_l c_1^l = 0 \quad (6)$$

where the coefficients d_l are functions of $a_{i,k}$, $a_{i,k+1}$, $b_{k,k+1}$, $\nu_{i,j}$, $\nu'_{i,j}$, and τ_j but are independent of the mass fractions c_i . It follows that the coefficients d_l can be computed once the temperature, density, and set of mass constraints are imposed. The calculated values of d_l can then be used in equation (6) along with the application of Newton's iteration scheme to find c_1 .

Newton's iteration scheme for determining c_1 can be written as

$$c_1(n+1) = c_1(n) - \frac{F(c_1(n))}{F'(c_1(n))} \quad (7)$$

where $c_1(n)$ is the n th approximation of c_1 and the derivative of $F(c_1)$ is

$$F'(c_1) = \sum_{l=1}^L l d_l c_1^{l-1} \quad (8)$$

The iteration scheme indicated by equation (7) is repeated until the required accuracy for c_1 is achieved. Equation (6) indicates that a number of roots are possible for c_1 . However, the correct value of c_1 must be within the range $0 \leq c_1 \leq 1$. If a root outside this range is obtained through the iteration process, it is eliminated and a different initial choice of c_1 is made to restart the iteration process. After a solution for c_1 is found within the range $0 \leq c_1 \leq 1$ through equation (7), the mass fractions

for all the other species, c_2, c_3, \dots, c_I , are found by direct substitution into the intermediate equations that lead to equation (6). (These intermediate equations are not shown for the general case but will be indicated for the specific example for a hydrogen-air model which follows.) Each value of the mass fractions, c_2, c_3, \dots, c_I , is examined to make certain it falls in the range from 0 to 1. The sum of all the mass fractions must also be unity. There is only one set of values for c_1 which satisfies these conditions.

Specific Equations for a Hydrogen-Air Gas Model

The application of the present technique for computing the chemical composition is best illustrated by a specific example of intermediate complexity. Consider an equilibrium system resulting from the combustion of pure hydrogen with air. Assume that air is a 4 to 1 molar mixture of N_2 and O_2 wherein the N_2 is taken as inert. The following seven species ($I = 7$), H, O, H_2 , O_2 , OH, H_2O , and N_2 with species index numbers $i = 1, 2, \dots, 7$, respectively, are assumed to appear in the system; the molecular weight of each of these species is taken to be 1, 16, 2, 32, 17, 18, and 28, respectively. These species are composed of three elements ($K = 3$), H, O, and N with element index numbers $k = 1, 2$, and 3, respectively. The two specific equations that result from equation (1) with $k = 1$ and $k = 2$ are, therefore,

$$\frac{c_1 + c_3 + \frac{1}{17} c_5 + \frac{1}{9} c_6}{c_2 + c_4 + \frac{16}{17} c_5 + \frac{8}{9} c_6} = b_{1,2} \quad (9)$$

and

$$\frac{c_2 + c_4 + \frac{16}{17} c_5 + \frac{8}{9} c_6}{c_7} = b_{2,3} = \frac{2}{7} \quad (10)$$

where $b_{1,2}$ is the arbitrary mass ratio of hydrogen to oxygen in the system and $b_{2,3} = \frac{2}{7}$ results from the assumption that air is a 4 to 1 molar ratio of N_2 to O_2 . In addition to these two equations, equation (2) applied to the present example leads to

$$c_1 + c_2 + c_3 + c_4 + c_5 + c_6 + c_7 = 1 \quad (11)$$

In addition to these three equations, there are $J = I - K = 4$ independent equilibrium expressions which result from the following independent chemical reactions,

$$\text{H}_2 = 2\text{H} \quad (\text{j} = 1)$$

$$\text{O}_2 = 2\text{O} \quad (\text{j} = 2)$$

$$\text{OH} = \text{O} + \text{H} \quad (\text{j} = 3)$$

$$\text{H}_2\text{O} = 2\text{H} + \text{O} \quad (\text{j} = 4)$$

Equation (3) then leads to the following equations where j has been set equal to 1, 2, 3, and 4,

$$c_3 = \tau_1 c_1^2 \quad (12)$$

$$c_4 = \tau_2 c_2^2 \quad (13)$$

$$c_5 = 17\tau_3 c_1 c_2 \quad (14)$$

$$c_6 = 9\tau_4 c_1^2 c_2 \quad (15)$$

(The arbitrary inclusion of the factors 17 and 9 in equations (14) and (15) makes for a somewhat simpler set of values for d_j , as will be shown. The only effect is to modify the relation between τ_j and $K_{p,j}$ shown by equation (5).) The quantities τ_j in these equations are related to the equilibrium constants in terms of partial pressures $K_{p,j}$ for each reaction through equation (5) and can be expressed explicitly as

$$\tau_1 = \frac{2\rho RT}{K_{p,1}} \quad (16)$$

$$\tau_2 = \frac{\rho RT}{8K_{p,2}} \quad (17)$$

$$\tau_3 = \frac{\rho RT}{16K_{p,3}} \quad (18)$$

$$\tau_4 = \frac{(\rho RT)^2}{8K_{p,4}} \quad (19)$$

where $K_{p,j}$ are functions of temperature alone. (The factors 17 and 9 in equations (14) and (15) have been accounted for in writing down equations (18) and (19). If these factors

were not used, then in what follows, it would be necessary to replace τ_3 by $17\tau_3$ and τ_4 by $9\tau_4$.)

It follows then that for a given temperature, density, and mass ratio of hydrogen to oxygen $b_{1,2}$, equations (9) to (15) constitute seven independent equations involving seven unknown quantities, c_1, c_2, \dots, c_7 . Equations (10) and (11) are combined to eliminate c_7 and equations (12) to (15) are then employed to eliminate c_3, c_4, c_5 , and c_6 to give

$$9\tau_2 c_2^2 + (74\tau_4 c_1^2 + 146\tau_3 c_1 + 9)c_2 + 2\tau_1 c_1^2 + 2c_1 - 2 = 0 \quad (20)$$

Equation (9) can also be reduced to contain only c_1 and c_2 by substitution of equations (12) to (15) so that

$$(\tau_4 c_1^2 + \tau_3 c_1)c_2 + \tau_1 c_1^2 + c_1 - \beta = 0 \quad (21)$$

where

$$\beta = \frac{2b_{1,2}}{2b_{1,2} + 9} \quad (22)$$

Equation (21) rearranges to give an explicit expression for c_2 in terms of c_1 only,

$$c_2 = \frac{\beta - \tau_1 c_1^2 - c_1}{\tau_4 c_1^2 + \tau_3 c_1} \quad (23)$$

This explicit expression for c_2 in terms of c_1 is then substituted into equation (20) to obtain a single equation that contains c_1 only. With some rearrangement, this expression containing c_1 only can be written as

$$F(c_1) = \sum_{l=0}^6 d_l c_1^l = 0 \quad (24)$$

where the coefficients d_l are

$$d_0 = \tau_2 \beta^2 \quad (24a)$$

$$d_1 = -(2\tau_2 - \tau_3)\beta \quad (24b)$$

$$d_2 = (\tau_2 - \tau_3) - (2\tau_1 \tau_2 - \tau_4)\beta + \frac{2}{9}(73\beta - 1)\tau_3^2 \quad (24c)$$

$$d_3 = \left(2\tau_1\tau_2 - \tau_1\tau_3 - 16\tau_3^2 - \tau_4 \right) + \frac{4}{9}(55\beta - 1)\tau_3\tau_4 \quad (24d)$$

$$d_4 = \left(\tau_1^2\tau_2 - \tau_1\tau_4 - 16\tau_1\tau_3^2 - 24\tau_3\tau_4 \right) + \frac{2}{9}(37\beta - 1)\tau_4^2 \quad (24e)$$

$$d_5 = -8\left(3\tau_1\tau_3\tau_4 + \tau_4^2 \right) \quad (24f)$$

$$d_6 = -8\tau_1\tau_4^2 \quad (24g)$$

A solution for c_1 can be obtained by application of equation (7) (Newton's iteration scheme) which yields

$$c_1(n+1) = c_1(n) - \frac{\sum_{l=0}^6 d_l c_1^l(n)}{\sum_{l=1}^6 l d_l c_1^{l-1}(n)} \quad (25)$$

wherein $c_1(n)$ is the n th approximation for c_1 and $c_1(n+1)$ is the next better approximation in this iteration scheme. The number of iterations required is, of course, dependent upon the accuracy desired.

For this specific example in which it has been assumed that air is a 4 to 1 molar mixture of N_2 and O_2 , and the mass ratio of hydrogen to oxygen is denoted by $b_{1,2}$, the possible range of c_1 is $0 \leq c_1 \leq \frac{b_{1,2}}{b_{1,2} + \frac{9}{2}}$. After a value of c_1 in this range has been

obtained through equation (25) with the desired accuracy, the value of c_2 can be computed directly from equation (23). Equations (12) to (15) are then employed to compute c_3 to c_6 , respectively. The value of c_7 is then computed by difference from equation (11). It should be noted again that all the values of c_i must each be within the range $0 \leq c_i \leq 1$.

The procedure for applying this technique to other systems would be the same as indicated in this specific case. As the system becomes more involved with respect to the number of species and reactions, the order of the series equivalent to equation (24) increases and it becomes increasingly more tedious to determine the coefficients d_l . This present technique is probably best suited to systems of intermediate complexity.

COMPARISON WITH OTHER METHODS

The purpose of this section is to compare the present method with other existing methods for computing the equilibrium chemical composition of reacting gas mixtures with particular regard for the speed of computation. As already mentioned, a study by Zeleznik and Gordon (ref. 1) has shown that none of the three most widely used general methods offer any significant computational advantages over the other. A comparison between only one of these methods and the present method is therefore all that is needed. The White method (ref. 4) which employs a free-energy minimization technique was selected for the purpose of making this comparison. The comparison to be made here is limited to determining the chemical composition at a given temperature and density for the two methods. It is recognized that solutions to problems are often required when two other thermodynamic quantities are specified. Where the latter is desired, the present method could become a part of an iteration scheme based on two thermodynamic quantities. It is believed that the most time-consuming step in all such schemes is the determination of the equilibrium composition; therefore, only the timing of this process will be considered.

Free-Energy Minimization Technique

The determination of the equilibrium chemical composition through the free-energy minimization technique requires the standard free energy of formation $\Delta F_{f,i}^0$ of each species in the mixture at the temperature of the mixture. The free energy of the mixture, which is a minimum at the equilibrium chemical composition, can be written as

$$\frac{F}{RT}(x_1, x_2, \dots, x_I) = \sum_{i=1}^I x_i \left(\frac{\Delta F_{f,i}^0}{RT} + \log_e p + \log_e \frac{x_i}{\bar{x}} \right) \quad (26)$$

where x_1, x_2, \dots, x_I represent a set of I mole numbers, x_i is defined as the moles of species i per gram of mixture, p is the total pressure expressed in atmospheres, and

$$\bar{x} = \sum_{i=1}^I x_i \quad (27)$$

The equilibrium chemical composition is determined when a set of mole numbers x_1, x_2, \dots, x_I produces a minimum value for the free energy of the mixture

$\frac{F}{RT}(x_1, x_2, \dots, x_I)$ given by equation (26) and at the same time satisfies the following mass balance expressions:

$$\sum_{i=1}^I \bar{a}_{i,k} x_i = \bar{b}_k \quad (k = 1, 2, \dots, K) \quad (28)$$

where $\bar{a}_{i,k}$ represents the number of atoms of element k contained in a molecule of species i , and \bar{b}_k is a constant equal to the total number of atomic weight units of element k per gram of mixture. Equation (26) when minimized within the limitations of equation (28) yields the chemical composition at a fixed T and p . Since the present method was developed for a fixed T and ρ , and a comparison between the two methods is desired, equation (26) is rewritten in terms of T and ρ . The equation of state of the mixture can be expressed as

$$p = \rho \frac{R}{W} T = \rho \bar{x} R T \quad (29)$$

Substitution of equation (29) for the pressure into equation (26) yields

$$\frac{F}{RT}(x_1, x_2, \dots, x_I) = \sum_{i=1}^I x_i \left[\frac{\Delta F_{f,i}^0}{RT} + \log_e \rho + \log_e(x_i) + \log_e RT \right] \quad (30)$$

wherein the units of R , where it is not a part of a nondimensional quantity, must be such that pressure takes on units of atmospheres. However, the appropriate quantity to minimize for a fixed T and ρ is no longer $\frac{F}{RT}(x_1, x_2, \dots, x_I)$, the Gibbs free energy, but rather $\frac{A}{RT}(x_1, x_2, \dots, x_I)$, the Helmholtz free energy. The relationship between the Gibbs molar free energy of species i , $\frac{F_i}{RT}$, and the Helmholtz molar free energy of species i , $\frac{A_i}{RT}$, is

$$\frac{F_i}{RT} = \frac{A_i}{RT} + 1 \quad (31)$$

Therefore, the expression to be minimized to find the equilibrium composition for a fixed T and ρ becomes

$$\frac{A}{RT}(x_1, x_2, \dots, x_I) = \sum_{i=1}^I x_i \left[\frac{\Delta F_{f,i}^0}{RT} + \log_e \rho + \log_e(x_i) + \log_e RT - 1 \right] \quad (32)$$

Since a machine program based on the minimization of equation (26) at constant p and T was available from a previous study, a program was not developed to use equation (32) at constant ρ and T directly. Instead, equation (26) was replaced by

equation (30) in the existing program and the input included fixed values of ρ and T . Since the existing program was set up for constant p , it follows that each iteration step is carried out for a constant pressure equal to that given by equation (29), but this pressure is modified from one iteration step to the next in direct proportion to \bar{x} . As the result approaches the correct solution, the pressure stabilizes. The computation time required for this solution was found to be essentially the same as that required when a given temperature and pressure were used directly in the program that utilized equation (26). The numerical results were also the same.

Input Quantities for Comparison

The input quantities for both the present method and the free-energy minimization technique include T , ρ , and a set of values for the molar standard-state free energy of formation of each species $\frac{\Delta F_{f,i}^0}{RT}$ at T . The free-energy method makes use of the quantity $\frac{\Delta F_{f,i}^0}{RT}$ directly in equation (30) whereas the present method utilizes $\frac{\Delta F_{f,i}^0}{RT}$ in computing equilibrium constants $K_{p,j}$ which are required in equation (5) for computing a set of values of τ_j . The relation between $K_{p,j}$ and $\frac{\Delta F_{f,i}^0}{RT}$ is

$$K_{p,j} = \exp \left[\sum_{i=1}^I (\nu_{i,j} - \nu'_{i,j}) \frac{\Delta F_{f,i}^0}{RT} \right] \quad (j = 1, 2, \dots, J) \quad (33)$$

In addition to these common quantities, the direct method requires an initial approximation for the mass fraction of H, that is, c_1 ; whereas the free-energy method requires an initial approximation for a set of mole numbers of all species. This set of mole numbers must, of course, be chosen to be consistent with the mass balance expressions given by equation (28).

The temperature and density chosen for comparison are $T = 4000^\circ \text{K}$ and $\rho = 3.0 \times 10^{-5} \text{ g/cc}$. At 4000°K the free-energy quantities $\frac{\Delta F_{f,i}^0}{RT}$ from reference 5 are

Species	$\frac{\Delta F_{f,i}^0}{RT}$	Species	$\frac{\Delta F_{f,i}^0}{RT}$
N_2	0	H	-0.46052
O_2	0	OH	-.52269
H_2	0	H_2O	-.54802
O	-.39144		

A stoichiometric mixture of H_2 and air, wherein air is assumed to be a 4 to 1 molar mixture of N_2 to O_2 , is used to define the mass balance. This definition requires that the quantity $b_{1,2}$ in equation (22) be set equal to 1/8 for the present method, and for the free-energy method, a suitable initial set of mole numbers is $x_{N_2}^0 = 0.0270270$,

$x_{O_2}^0 = 0.0067568$, $x_{H_2}^0 = 0.0135135$, and $x_O^0 = x_H^0 = x_{OH}^0 = x_{H_2O}^0 = 10^{-9}$. This set corresponds to a 1:2:4 molar mixture of $O_2:H_2:N_2$ in a reference state. Because the program for the free-energy minimization technique requires initial nonzero values for all species considered in the mixture, the reference values for the mole numbers of O, H, OH, and H_2O were chosen to be outside the eight significant number range but nonzero. The present method requires an initial estimate of the mass fraction of only one species and a value of zero is chosen for the mass fraction of atomic hydrogen, c_1 . The results of the calculations by the two methods are discussed in the next section.

RESULTS AND DISCUSSION

The present method and the free-energy minimization technique for computing the chemical composition of the aforementioned hydrogen-air mixture were programed in FORTRAN IV. A number of runs were made using these two programs on an IBM 7094 computer at the Langley Research Center. These computations were made at a temperature of $4000^\circ K$, total density of 3×10^{-5} g/cc, and a stoichiometric mixture of hydrogen in air (4 to 1 molar ratio of N_2 to O_2). The accuracy criterion for each method was adjusted so that the hydrogen atom mass fraction would be calculated to five-place accuracy for both methods. The calculated results for these two methods, expressed in terms of mass fraction of each species, are listed in table I. The variations in the accuracy between the two methods are indicated by underscoring.

TABLE I.- EQUILIBRIUM MASS FRACTIONS FOR SPECIES IN STOICHIOMETRIC HYDROGEN-AIR MIXTURE FOR TWO COMPUTATIONAL METHODS

$$[T = 4000^\circ K \text{ and } \rho = 3 \times 10^{-5} \text{ g/cc}]$$

Species	Present method	Free-energy minimization technique
N_2	0.75675 <u>675</u>	0.75675599
O_2	.163563 <u>38</u> $\times 10^{-1}$.1635654 <u>5</u> $\times 10^{-1}$
H_2	.358592 <u>37</u> $\times 10^{-2}$.358591 <u>71</u> $\times 10^{-2}$
O	.170506 <u>37</u>	.17050748
H	.213864 <u>73</u> $\times 10^{-1}$.2138645 <u>3</u> $\times 10^{-1}$
OH	.274475 <u>68</u> $\times 10^{-1}$.2744771 <u>6</u> $\times 10^{-1}$
H_2O	.396060 <u>28</u> $\times 10^{-2}$.396062 <u>00</u> $\times 10^{-2}$

After it had been established that the two methods give the same numerical result within the same order of accuracy, a number of computational runs were made to compare the speed of calculation for each method. The timing technique available for this study permitted only a determination of the total running time for an arbitrary number of cases. This total time is composed of three parts: the input time t_{in} , the actual computational time t_c , and the output time t_{out} . The computational time for N identical cases can be expressed as the product of N and the computation speed m

$$t_c = Nm \quad (34)$$

and the total machine time is

$$t_T = t_{in} + Nm + t_{out} \quad (35)$$

The quantity of interest in this study is m , the actual computational speed for each method; however, only t_T is measured directly while N is an input value. One way of determining m is to obtain values of t_T over a range of N for conditions such that $Nm \gg t_{out}$ and $Nm \gg t_{in}$. In this study the program was allowed to run for a given N without an output so that $t_{out} = 0$. This procedure was followed after the two methods were shown to yield the same solution to the same order of accuracy as indicated in table I. The second condition, $Nm \gg t_{in}$, was achieved by measuring t_T for a very large number of cases, N .

The results for a series of timed machine calculations for both the present method and the free-energy minimization technique are presented in figure 1. The total machine running time t_T is plotted as a function of the number of cases run N for the free-energy minimization technique and for the present method. The previously mentioned initial set of mole numbers were used for the free-energy minimization technique which, in turn, required 12 iterations to find the solution. These results are represented by the uppermost curve where N ranges from 500 to 8000. It is seen that the slope of this curve has reached unity for $N \geq 6000$; thus, in this region, the unit computational time is

$$m = \frac{t_T}{N} \quad (Nm \gg t_{in}, t_{out} = 0) \quad (36)$$

The unit computational time m is, of course, independent of both t_T and N so that the value of m determined in this manner is the time per unit case for any number of cases run. The value of m for the free-energy minimization technique requiring 12 iterations is seen from figure 1 to be 252 msec/case. The deviation from unit slope for the lower values of N on this curve is due to the increasing importance of the input time t_{in} relative to Nm as N decreases.

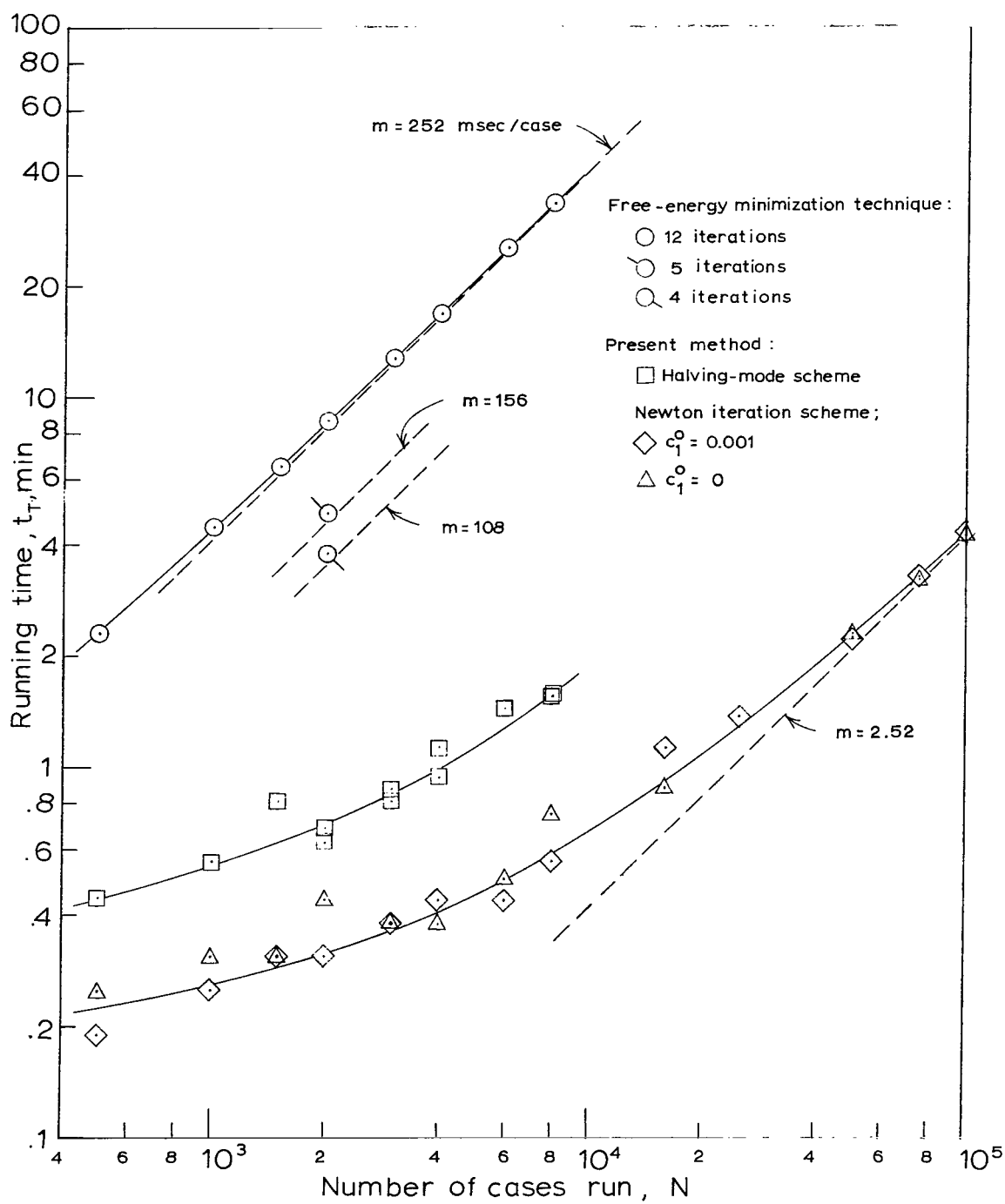


Figure 1.- Comparison of running times for free-energy minimization technique and present method.

The free-energy minimization technique was also timed for two additional runs for which the initial set of mole numbers were chosen to be much closer to the ultimate values. The number of cases run N for each of these two runs were 2000. One of these runs resulted in 5 iterations, while a run for a still more accurate initial set of mole numbers resulted in 4 iterations. These two runs are also shown. All the effect of t_{in} has not been eliminated in these two runs so that the value of m for each was estimated by drawing in a line of unit slope displaced slightly below each data point to approximate the influence of t_{in} . The run requiring 5 iterations resulted in a unit computational time of 156 msec/case and the run requiring 4 iterations gave $m = 108$. It should be mentioned that the runs that required only 4 or 5 iterations resulted from more accurate initial sets of mole numbers. The series of runs in which 12 iterations were required is probably a more practical basis for comparison.

The present method of calculation was also timed for a series of runs for the same computational conditions, that is, no output time ($t_{out} = 0$) and over a range of N with N reaching large values. A series of runs were made for each of two different iteration schemes. The results for a halving-mode* iteration scheme is shown for the range $500 \leq N \leq 8000$. The scattering of the data points is due to uncontrollable but slight variations in t_{in} from run to run. The total running time even at $N = 8000$ is still strongly influenced by the input time; therefore an accurate evaluation of m is not attempted. The value of m would, however, be less than 12 msec/case. An accurate value of m could be obtained by making computations for still larger values of N . This was not done because the halving-mode scheme is not one of the most timewise efficient iteration schemes. Instead, the Newton iteration scheme indicated by equation (7) was used to complete the comparison.

The lowest curve in figure 1 shows the results for the present method using the Newton iteration scheme. A series of runs were carried out for an initial value of c_1 equal to 0.001 and another series for an initial value of zero. Within the scatter of the data, which again is due to slight variations in t_{in} from run to run, the two initial values

*The halving-mode scheme makes use of equation (24) directly. Initial values of c_1 equal to 0, 0.5, and 1.0 are used to evaluate $F(c_1)$. The interval in which a sign change in $F(c_1)$ is noted is then assumed to contain the desired root. The midpoint of this new and more limited interval is then computed and used to seek a more narrow interval by observing a sign change in $F(c_1)$. This procedure is repeated until the desired accuracy is achieved. If more than one root exists in the region $0 \leq c_1 \leq 1.0$, the iteration scheme must account for this. There is, of course, only one root c_1 that satisfies all the other equations whereas all values of c_i are real and positive.

of c_1 produced the same curve. In these series of runs it was necessary to make N as large as 10^5 in order to satisfy the condition that $Nm \gg t_{in}$. A slope of unity is essentially achieved when $N = 10^5$ so that $m = 2.52$ msec/case. This unit computation time m for the present method using the Newton iteration scheme is two orders of magnitude less than that for the free-energy minimization technique with 12 iterations. This comparison is for the same order of accuracy in the composition for each method, as well as the same input quantities.

The free-energy minimization technique and the other general methods for computing the equilibrium chemical composition of reacting mixtures can of course be used for a large range of reacting gas mixtures with a very large number of species and elements. This generality offers a great advantage whereas the present method is limited to the species and elements (not their relative amounts) that have been chosen to develop the iteration equations. The advantage of the present method over the more general methods is realized when machine computation time is important, for example, when a finite-difference calculation network requires a very large number of equilibrium composition calculations. The computations necessary to determine the equilibrium chemical composition from point to point in certain flow field calculations often require excessive machine time so that a series of empirical curve fits of the equilibrium thermodynamic quantities are used to achieve a more reasonable machine time. This representation of the thermodynamic quantities is limited to the specific gas model for which it was developed. If the present method is used, account could be made for the point to point change in the elemental distribution due to diffusion by allowing the quantities $b_{1,2}, b_{2,3}, \dots$ in equation (1) to be variables determined by the appropriate diffusion equations.

It is noted that the present method offers considerable advantage over the more general method with regard to machine computation time. This advantage has been achieved at the expense of loss of generality. The comparison herein was based on a hydrogen-air gas model which represents a system of intermediate complexity. Other systems of similar complexity could likewise be formulated and used in conjunction with the present method. It is possible to apply this technique to more complex systems. It does not seem practical, however, to extend this present method to very complex systems because the algebraic manipulation becomes overwhelmingly tedious as the number of species and/or elements in the system become very large. For this reason, the practical application of the present method is probably limited to systems of intermediate complexity like the system studied or perhaps only somewhat more complex.

CONCLUDING REMARKS

A method for computing the chemical composition of reacting gas mixtures has been presented that shows considerable advantage with respect to machine computation time. For the particular comparison considered herein, the unit computational speed for this method is two orders of magnitude faster than the more general and most commonly used computation schemes. This advantage is achieved by reducing the system of equations down to one equation containing a single unknown. This reduction to one equation involves much tedious algebra, but the procedure is believed to be worthwhile when computational time must be kept short and when a large number of computations are required for the same chemical system. The application of the present method to machine computations requires that a new set of equations be developed for each chemical system that contains a different set of chemical species. The relative total mass of each element in the system can be treated as variable input.

The great advantage in computational speed noted was based on a comparison wherein the chemical system was of intermediate complexity. It is believed that chemical systems of greater complexity would also show this advantage in computational speed, but the effort required to reduce the system of equations to the necessary single expression may be the limiting factor for very complex systems.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., March 16, 1966.

APPENDIX

REDUCTION OF WORKING EQUATIONS TO A SINGLE EQUATION CONTAINING A SINGLE UNKNOWN

The substitution of the J equilibrium expressions indicated by equation (3) into the K conservation of mass expressions indicated by equations (1) and (2) yields K equations which contain only K unknown mass-fraction variables. These K equations can be written in general form as

$$\sum_{m=0}^{M_n} A_{m,n} c_{\alpha}^m = 0 \quad (n = 1, 2, \dots, K) \quad (A1)$$

where c_{α} denotes the mass fraction of a particular species which is one of the K mass-fraction variables in these K equations, M_n is the highest order of c_{α} in the n th equation, and $A_{m,n}$ is a polynomial function of the remaining $K - 1$ mass-fraction variables from which c_{α} is excluded, as well as a function of the known quantities τ_j , $a_{i,k}$, $\nu_{i,j}$, $\nu'_{i,j}$, and $b_{k,k+1}$.

Equation (A1) can be divided through by either $A_{0,n}$ or $A_{M_n,n}$ to give either

$$1 + \sum_{m=1}^{M_n} \frac{A_{m,n}}{A_{0,n}} c_{\alpha}^m = 0 \quad (n = 1, 2, \dots, K) \quad (A2)$$

or

$$c_{\alpha}^{M_n} + \sum_{m=0}^{M_n-1} \frac{A_{m,n}}{A_{M_n,n}} c_{\alpha}^m = 0 \quad (n = 1, 2, \dots, K) \quad (A3)$$

Consider equation (A2) first with $n = 1$ and then with $n = 2$ so that

$$1 + \sum_{m=1}^{M_1} \frac{A_{m,1}}{A_{0,1}} c_{\alpha}^m = 0 \quad (A4)$$

and

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$$1 + \sum_{m=1}^{M_2} \frac{A_{m,2}}{A_{0,2}} c_{\alpha}^m = 0 \quad (\text{A5})$$

If the choice of equations with $n = 1$ and $n = 2$ is made so that $M_1 \geq M_2$, subtraction of equation (A5) from equation (A4) yields

$$\sum_{m=1}^{M_1} \left(\frac{A_{m,1}}{A_{0,1}} - \frac{A_{m,2}}{A_{0,2}} \right) c_{\alpha}^m = 0 \quad (\text{A6})$$

or

$$\sum_{m=0}^{M_1-1} \left(A_{m+1,1} A_{0,2} - A_{m+1,2} A_{0,1} \right) c_{\alpha}^m = 0 \quad (\text{A7})$$

Note that if the m th power on c_{α} does not exist in the n th equation, then $A_{m,n}$ is zero for that particular case.

Consider equation (A3) first with $n = 1$ and then with $n = 2$ so that

$$c_{\alpha}^{M_1} + \sum_{m=0}^{M_1-1} \frac{A_{m,1}}{A_{M_1,1}} c_{\alpha}^m = 0 \quad (\text{A8})$$

and

$$c_{\alpha}^{M_2} + \sum_{m=0}^{M_2-1} \frac{A_{m,2}}{A_{M_2,2}} c_{\alpha}^m = 0 \quad (\text{A9})$$

If $M_1 = M_2$, subtraction of equation (A9) from equation (A8) yields

$$\sum_{m=0}^{M_1-1} \left(\frac{A_{m,1}}{A_{M_1,1}} - \frac{A_{m,2}}{A_{M_2,2}} \right) c_{\alpha}^m = 0 \quad (\text{A10})$$

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or

$$\sum_{m=0}^{M_1-1} (A_{m,1}A_{M_2,2} - A_{m,2}A_{M_1,1})c_{\alpha}^m = 0 \quad (A11)$$

For the case where $M_1 = M_2$, equations (A7) and (A11) represent two independent equations in which the highest order of c_{α} is $M_1 - 1$ rather than M_1 as it was in equation (A1) for $n = 1$ and $n = 2$. However, if $M_1 > M_2$, equation (A7) is still obtained, but instead of using equation (A11), equation (A1) with $n = 2$ is used unchanged,

$$\sum_{m=0}^{M_2} A_{m,2}c_{\alpha}^m = 0 \quad (A12)$$

For this case where $M_1 > M_2$, equations (A7) and (A12) represent two independent equations in which the highest order of c_{α} is $M_1 - 1$. In either case, the coefficients in equation (A7) and in equation (A11) or (A12) are polynomials which can be redefined for convenience so that

$$\sum_{m=0}^{M_1-1} B_{m,1}c_{\alpha}^m = 0 \quad (A13)$$

and

$$\sum_{m=0}^{M_2} B_{m,2}c_{\alpha}^m = 0 \quad (A14)$$

The procedure to this point is now repeated by starting with equation (A1) but with a different pair, for example, $n = 3$ and $n = 4$. If K is odd, one of the n original equations indicated by equation (A1) will be used twice so that only one independent equation is developed from that pair. A general expression for these reduced equations, which includes equations (A13) and (A14) as special cases, can be written as

$$\sum_{m=0}^{M_n-1} B_{m,n}c_{\alpha}^m = 0 \quad (n = 1, 2, \dots, K) \quad (A15)$$

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Because this equation is of the same form as equation (A1), it follows that the order of these K equations can ultimately be reduced to first order with respect to c_α , that is,

$$Q_{1,n}c_\alpha + Q_{0,n} = 0 \quad (n = 1, 2, \dots, K) \quad (A16)$$

where $Q_{1,n}$ and $Q_{0,n}$ are involved polynomial functions of $K - 1$ mass-fraction variables excluding c_α .

The variable c_α can be eliminated from equation (A16) to give the following $K - 1$ equations which do not contain c_α .

$$Q_{0,n}Q_{1,n+1} - Q_{1,n}Q_{0,n+1} = 0 \quad (n = 1, 2, \dots, K-1) \quad (A17)$$

Equation (A17) can now be written in the form

$$\sum_{m=0}^{M'_n} A'_{m,n} c_\beta^m = 0 \quad (n = 1, 2, \dots, K-1) \quad (A18)$$

wherein c_β is the mass fraction of one of the remaining $K - 1$ species, M'_n is the highest order of c_β for the n th equation, and $A'_{m,n}$ are polynomial functions of $K - 2$ mass-fraction variables excluding c_β , as well as functions of the known quantities τ_j , $a_{i,k}$, $\nu_{i,j}$, $\nu'_{i,j}$, and $b_{k,k+1}$.

Equation (A18) represents $K - 1$ equations which contain $K - 1$ mass-fraction variables. The reduction procedure used to obtain equation (A18) which represents $K - 1$ equations and unknowns by starting with equation (A1) which represents K equations and unknowns can be used as many times as is necessary to obtain a single polynomial expression involving only one mass-fraction variable, for example, c_1 ,

$$\sum_{l=0}^L d_l c_1^l = 0 \quad (A19)$$

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